InLCA: Case Studies – Using LCA to Compare Alternatives

Applying Life Cycle Tools and Process Engineering to Determine the Most Adequate Treatment Process Conditions. A Tool in Environmental Policy

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Abstract

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Background. The analysis of a wastewater treatment technology, under a expanded boundaries system which includes both the technology and the inputs required for its operation, quantifies the overall environmental impact that may result from the treatment of a wastewater stream. This is particularly useful for environmental policy makers being that a expanded boundaries system tends to provide a holistic view. The former view can be highly enriched with the use of process engineering tools, such as mathematical process modelling, process design, performance assessment and cost optimised models.

Main Features. The traditional approach used to assess waste treatment technologies is contrasted with a life cycle analysis (LCA) approach. The optimal design of a granular activated carbon adsorption (GAC) process is used as a model system to demonstrate the advantages of LCA approaches over traditional approaches. Further sections of the paper describe a mathematical framework for the assessment of technologies, design considerations applied in the cost optimised carbon adsorption model, the use of LCA techniques to perform an inventory of all emissions associated to the process system and, some of its environmental impacts.

Results. Economic and environmental considerations regarding the optimum process design are introduced as a basis for decision towards the selection and operating conditions of wastewater treatment technologies. Moreover, the use of LCA has revealed that the environmental burden associated with the wastewater treatment may produce a higher environmental impact than one that can be caused by untreated discharges.

Conclusion. The paper highlights the string advantages that environmental policy makers may have by combining LCA and process engineering tools. Furthermore, this approach can be incorporated into other existing treatment processes or for process designers.

Keywords: Life Cycle Assessment (LCA); Granulate Activated Carbon (GAC) adsorption; process engineering and design; Volatile Organic Compounds (VOCs); wastewater treatment

Introduction

One of the main objectives of sustainable engineering is to deal with waste streams, with the objective of achieving environmental benefits, economic optimisation and societal acceptability [1]. The rapid development of process industries has given rise to multiple environmental problems which, in some cases, have lead to the development of cleaner technologies and waste minimisation techniques. These initiatives tend to ameliorate pollution problems by using, or generating, lower amounts or less harmful pollutants. However, waste minimisation techniques and cleaner technologies have not been able to totally eliminate the discharge of pollutants into the environment, therefore, treatment of pollutants at the end-of-the-pipe is still a common practice among process industries. This situation leads to the identification of the best option among several process routes, design options, process conditions and technologies. One alternative to deal with this situation is to perform a sustainability evaluation [2].

The sustainability of any process or technology requires waving the traditional evaluation scheme in which environmental constraints (discharge limits) are satisfied at minimum economic cost. Current sustainability assessments include considerations towards economic, environmental and social impacts [2]. However, deciding on the most adequate technology or process is not crystal clear since trade-offs among economic, environmental and social impacts usually appear. Furthermore, process performance differs depending on the type of environmental impact that is analysed and the boundaries defined for the assessment [3].

The hypothesis behind this paper is the environmental impact caused by a treatment process may, under certain conditions, be greater than the environmental impact generated by the wastewater emissions. Romero-Hernandez et al described trade-offs between decreasing environmental impact due to wastewater emissions and increasing environmental impact associated with inputs to the wastewater treatment process, such as electricity, steam and raw materials [3]. This work is based on the use of LCA as a methodology to assess the environmental impacts of a product or process. Under this methodology, a consistent system boundary around the wastewater process is defined so that all wastes associated with the process (i.e., electricity, raw materials generation, steam and steel production), are included when the inventory of emissions is performed [4]. This approach has been successfully incorporated into process analysis and design [5,6] and constitutes a wide area of research.

In order to explore the use of life cycle tools and process engineering for the assessment of technologies, the author has studied a widely used end-of-the-pipe treatment tech-

nology: granular activated carbon adsorption. This process is considered as one of the most effective methods of controlling emissions of volatile organic compounds, VOCs, a class of pollutant that is often present in industrial wastewater streams [7]. Granular carbon offers great pollutant flexibility and its potential to eliminate organic contaminants from water, has made carbon adsorption a yardstick by which other treatment technologies and industrial processes can be evaluated [8].

The following sections describe a general mathematical framework which embraces design considerations applied in the cost optimised carbon adsorption model, the use of LCA techniques to perform an inventory of all emissions associated to the process system and its environmental impacts.

1 General Framework for Technology Assessment

The main steps to be performed in order to analyse a treatment technology from an economic and environmental point of view are presented below while a schematic representation of the integrated approach is presented in **Fig. 1**.

(i) **Characterize the flow rate and the concentration of the pollutants in the wastewater.**

(ii) **Develop cost optimised models** for wastewater treatment technologies, which can be used to find complete mass and energy balances for the processes, at the cost optimal point (which will depend upon the discharge constraints).

(iii) **Generate an inventory of pollutants** including both emissions arising due to incomplete abatement and discharges associated with process inputs. This should be based on a Life Cycle Assessment (LCA) approach. This activity helps to compare the environmental performance of each wastewater treatment technology, based on the relationship between emissions associated to *Outputs* (waste streams arriving from the process) and *Inputs* (i.e., emissions generated from the production of electricity, steam, steel, etc., that are required in order to operate the process).

(iv) **Assess the environmental impact of the entire system** using appropriate environmental metrics. This will help to identify the optimal degrees of pollution abatement (ODPAs), at which environmental impact is minimized. Moreover, it shall assist in the identification of the most adequate technology, process conditions or design.

1.1 Mathematical model

The first part of the integrated approach consists of defining the inlet parameters (flow and concentration) and the maximum amount of pollutant that can be discharged without posing significant risk to the environment. These values provide an indication of the minimum amount of pollutant that needs to be removed by the wastewater treatment technology. The second part of this approach deals with the design and evaluation of wastewater treatment technologies. Wastewater treatment processes are represented by a set of mathematical equations which describe the properties of the inlet waste stream, equipment specifications, cost functions and the degree of pollutant removal. The concept of ***removal efficiency*** is incorporated into the model as a parameter describing the amount of pollutant removed in relation to its initial concentration. The system assumes **n** number of pollutant species regulated by emission limits and **m** number of pollutant species associated with inputs generation. The set of removal efficiencies is defined by η, which is a vector with **n** number of removal efficiencies applied to each pollutant specie, $\eta=[\eta_1, \eta_2,...,\eta_n]$. Therefore, the mathematical model consists of a series of specified parameters, such as the inlet flowrate and the initial concentration of pollutant in the wastewater stream (assumed to be fixed by the production process), and removal efficiencies (which are directly related to the emission limits imposed by legislation) which are incorporated into a cost optimization program.

This optimization identifies the process design that minimizes cost of abatement, *Cost(d, x)*, for a given set of discharge limits, η and equality and inequality constraints, $h(d,x)=0$ and $g(d,x)\leq 0$, which represent design specifications, mass and energy balances. Index *d* denotes the potential existence of equipment units while *x* corresponds to design variables and operating conditions.

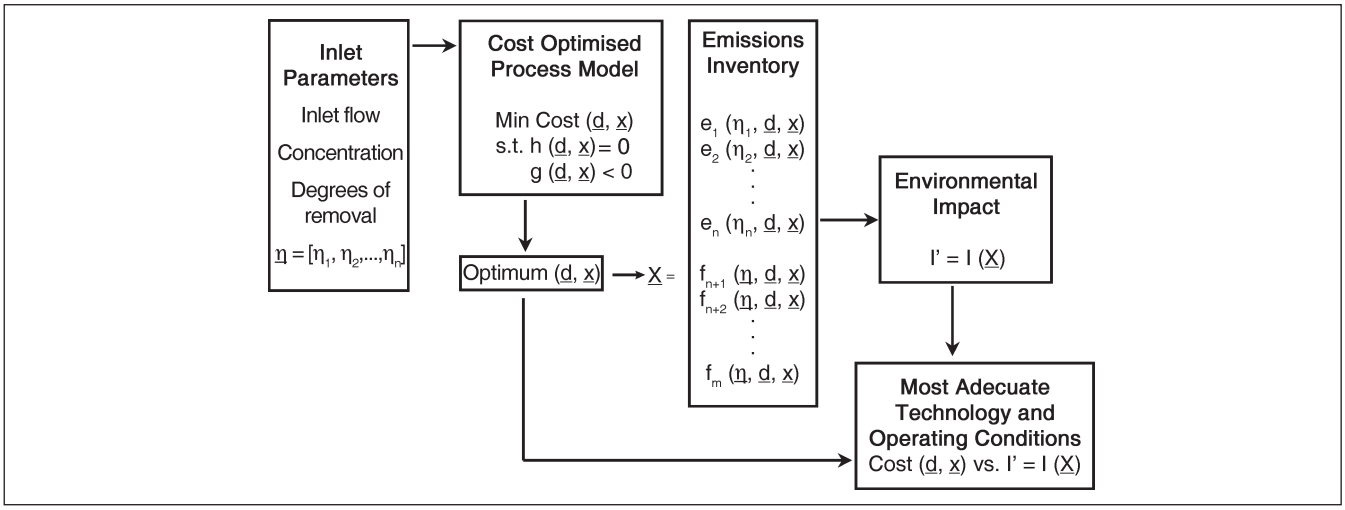

Fig. 1: Schematic representation of the integrated approach used to identify conditions at which minimum cost of treatment and minimum environmental impact occur

Two outputs emerge from the technology optimization program:

1. The minimum cost and the optimum design and operating conditions to achieve the specified emission limits, *Cost(d, x)*.
2. A vector of total emissions, **X**, determined at the cost optimal configuration. It comprises both emission of pollutants from the wastewater stream, also called ***Outputs***, $e_{i\ (i=1,\ldots,n)}$, and emission of pollutants associated with ***Inputs,*** $f_{i\ (i=n+1,\ldots,m)}$:

$$\mathbf{X} = [\, e_1, e_2, \ldots, e_n, f_{n+1}, f_{n+2}, \ldots, f_m] \quad (1)$$

The environmental impact of the system is then related to **X** through an environmental function, **I'=I(X)**. Any type of environmental impact (i.e., global warming, ozone depletion, ozone creation, critical air volumes, etc.) can be incorporated into this function, usually with the use of environmental indices, *EI*, for each pollutant species, *i*. Given that each index describes a specific environmental impact per unit of mass of pollutant species, it allows all emissions from different compounds to be lumped together into a single number, which represents the specific impact. Thus, the environmental function, is expressed as the sum of environmental impacts generated by both *Outputs* and *Inputs* from each pollutant species, *i*, and can be described as follows:

$$\mathbf{I}(\underline{\mathbf{X}}) = \sum_{i=1}^{n} e_i(\eta_i, X) EI_i + \sum_{i=n+1}^{m} f_i(\eta_i, X) EI_i \quad (2)$$

The previous mathematical model is a robust tool that can be used for decision making in environmental policy and technology management. The justification for using this approach, in which treatment costs are minimized subject to discharge constraints, is simply that this is a typical industrial response to environmental legislation. The mathematical model considers the environmental impact of the process, and an iterative process can be carried out by varying the emission limits, within regulated values, until the optimal conditions, at which the minimum environmental impact occurs, are identified. Therefore, the main outputs that emerge from this approach are the maximum load of pollutants that can be discharged into the environment; the optimal operating conditions and configuration for a wastewater treatment technology. These sets of condition incur a minimum treatment cost and; the minimum environment impact that can be achieved due to the treatment of wastewater discharges.

The following section illustrates the use of LCA and Process Engineering to assess the design and operation of a clean up technology.

2 Carbon Adsorption Technology

There are several process configurations associated with the design of an activated carbon adsorption process. This paper presents a cost optimised process model developed for a downflow fixed-bed pressured system, operating with two columns in series and granular activated carbon (GAC) as the adsorbent. This configuration has been acknowledged as the most common adsorption option for industrial water treatment applications, since it is convenient for the treatment of relatively small flowrates of wastewater, with moderate concentration of organics and achieves high degrees of removal [7,9].

2.1 Process description

The carbon adsorption process designed for this work is illustrated in **Fig. 2**. Wastewater is pumped into the top of a first adsorber column, where organic compounds are removed as they pass through the column. Then, the stream is fed to the top of a second adsorber column and leaves from the bottom as a stream minimized of pollutant. When saturation in the first column occurs, the adsorber is disconnected from the process and the wastewater enters only into the second adsorber. The carbon in the first adsorber is removed through an hydraulic pumping system and sent to a spent carbon storage container for regeneration. Once the column has been replenished with virgin or regenerated carbon, it is connected as the second adsorber. The carbon replacement process is repeated once the second column is exhausted.

Adsorption columns and thus, the amount of GAC required for the process are the most important considerations for process design. They both dictate the specifications for further equipment including pumps, eductors and storage tanks. This process model is based on the ideas presented by Crittenden, et al and Hand since their procedures have been applied successfully for the design of carbon adsorption columns [10,11,12]. The constant-pattern-homogeneous-surface-diffusion-model developed by Hand was used to predict liquid phase GAC usage rates for selected organics. The activated carbon adsorption calculations performed in this work assume two inlet flow scenarios:

1. A wastewater flow of **10 m³/h containing 1000 g/m³ of benzene** and,
2. a wastewater flow of **10 m³/h containing 1000 g/m³ 1–2 dichloroethane (DCE)**.

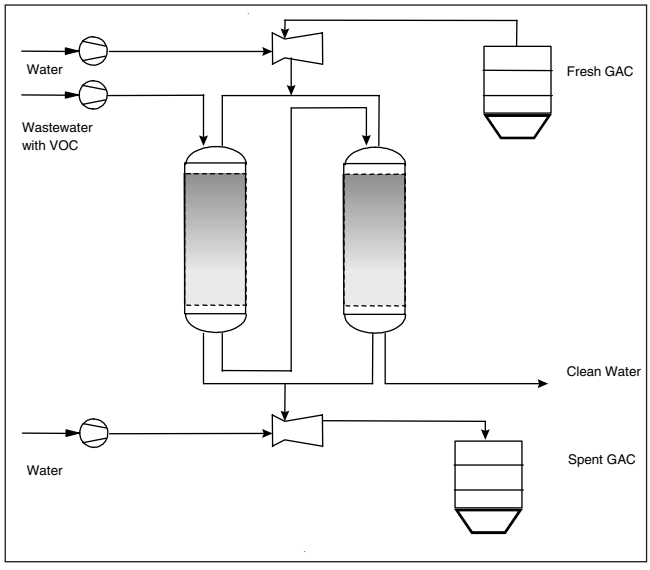

Fig. 2: Carbon adsorption process

3 Process Engineering: Cost Optimised Model

The mathematical model consists of 36 equations, 37 variables and 1 degree of freedom (*mass throughput*, which is the ratio of mass fed compared to the mass required to saturate the adsorber). It has been solved with the use of an optimisation tool. The general algebraic modelling system (GAMS) was employed to obtain the optimal cost design for the carbon adsorption process and the environmental impacts that may result from its operation. In order to illustrate in detail the steps for a model formulation, **Appendix A** presents a complete description of the carbon adsorption process design and modelling (Online only, go to: http://dx.doi.org/10.1065/lca2004.09.180.11).

The unsteady state nature of the carbon adsorption process requires an expression to relate the amount of pollutant removed with respect to the volume of wastewater fed into the process. The GAC process model developed in this work assumes that there are two adsorption columns connected in series. According to the optimal process design and the breakthrough curves shown in **Fig. 3a** and **Fig. 3b**, the first column initially removes almost all the pollutant, while the second column removes the traces of pollutants that are not treated in the first column.

Breakthrough curves show that the adsorption zone is narrow enough (width of δ) so that it stays within the column. Moreover, the curves do not spread out as the adsorption zone moves down the column, but retain a constant pattern. Just before saturation occurs in column 1, it is disconnected and wastewater is fed directly to the second column, which removes most of the pollutant. The carbon from column 1 is replaced, and it is re-connected to receive the wastewater from column 2. So long as the height of the column is several times greater than δ, **breakthrough in concentration never occurs** and pollutant removal is practically 100%. This result is consistent with results presented in other publications, which show that small slope values in the Freundlich isotherm, typical from hydrophobic compounds such as benzene and DCE, present relatively sharp breakthrough curves, particularly for single-solute systems such as those studied in this work [7].

Total costs of treatment are estimated as a function of capital and operating cost. The equipment contributing to capital cost includes: 2 adsorber columns, the wastewater pump, two pump-eductor systems for carbon transportation, and two storage tanks for fresh and exhausted GAC. Conversely, operating costs are a function of the electricity consumed to run the process pumps, water required to transport the GAC and replacement of GAC employed for the process. Due to the relatively low volume of GAC employed, regeneration was considered to be performed off-site. In other words, the company that served as a platform for this case study doesn't pay directly for regeneration, permits or disposal. However, it is important to note that these costs are considered being that suppliers of GAC include it on the price.

Costs for the main components of the GAC wastewater treatment process are presented in **Table 1**. The main equipment items are the feed pump, the pump-eductor systems, the adsorption column and the storage tanks.

Table 1: Cost of treatment for the carbon adsorption process

Cost	Benzene	DCE
Total Cost (£/yr)	459,120	511,470
Capital Cost (£/yr)	103,550	100,730
Operating Cost (£/yr)	355,560	410,740
Cost of Adsorbers (£/yr)	30,640	27,235
Height (m)	2.617	2.267
Diameter (m)	1.614	1.614
Cost of Storage Tanks (£/yr)	57,198	58,947
Cost of Feed Pump and Eductors (£/yr)	6,825	6,646
Cost of GAC (£/yr)	352,580	407,500
GAC (kg/yr)	248,296	286,971
Load Ratio kg_{VOC}/kg_{GAC}	0.328	0.284
Cost of Electricity (£/yr)	2,721	2,852
Electricity (kw.hr/yr)	54,420	57,040
Cost of Water (£/yr)	260	384

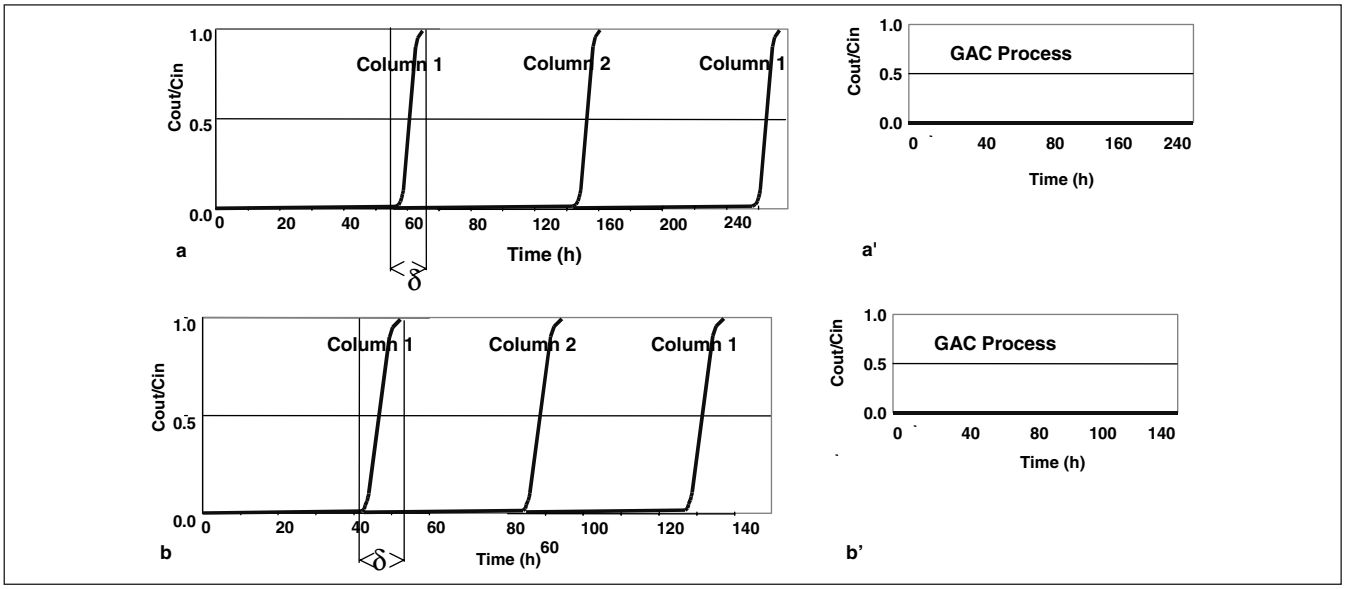

Fig. 3a and 3b: Breakthrough curves for the adsorption of benzene and DCE in GAC

Characteristics of the feed pump are affected by the flowrate, the nature of the liquid and the head required. In this model, the inlet flowrate is assumed to be constant during the process operation. Since benzene and DCE are present in the wastewater stream at low concentrations the viscosity and density of the inlet stream were assumed to be those of pure water. Therefore, the power requirements for the feed pump are only dictated by the height of the adsorption columns. The design of pump-eductor systems is affected by the flow of water required to convert the GAC into slurry and by the operating time of this intermittent system. Nonetheless, both previously mentioned variables depend directly on the amount of GAC required for the wastewater treatment process.

The adsorption columns and the storage tanks are the equipment items that resulted most significantly affected by the process design. Both items are directly related to the amount of GAC required for the process. As expected, the adsorptive capacity of the carbon to attract organics is a very sensitive variable, since it determines the amount of GAC needed to achieve water purification and the height of the adsorption columns.

Although the amount of GAC required also influences the size and electricity requirements of pumps and eductors, its impact is relatively small compared to the columns and the storage tanks. In general, a higher adsorption column, leads to a smaller number of GAC exchanges per year but it also leads to higher electricity requirements of the inlet pump.

The amount of GAC required for the process is the most significant cost component, and **represents more than 75% of total costs**. This amount is related to the Freundlich Isotherm constants, and the inlet concentration for each organic compound in water. Sensitivity analyses were carried out in order to determine the relative influence of K, $1/n$, and C_{in}.

As shown in **Fig. 4** by single-component adsorption isotherms and the process model, K relates the adsorbability of the contaminant (mass pollutant adsorbed/mass of GAC), whereas

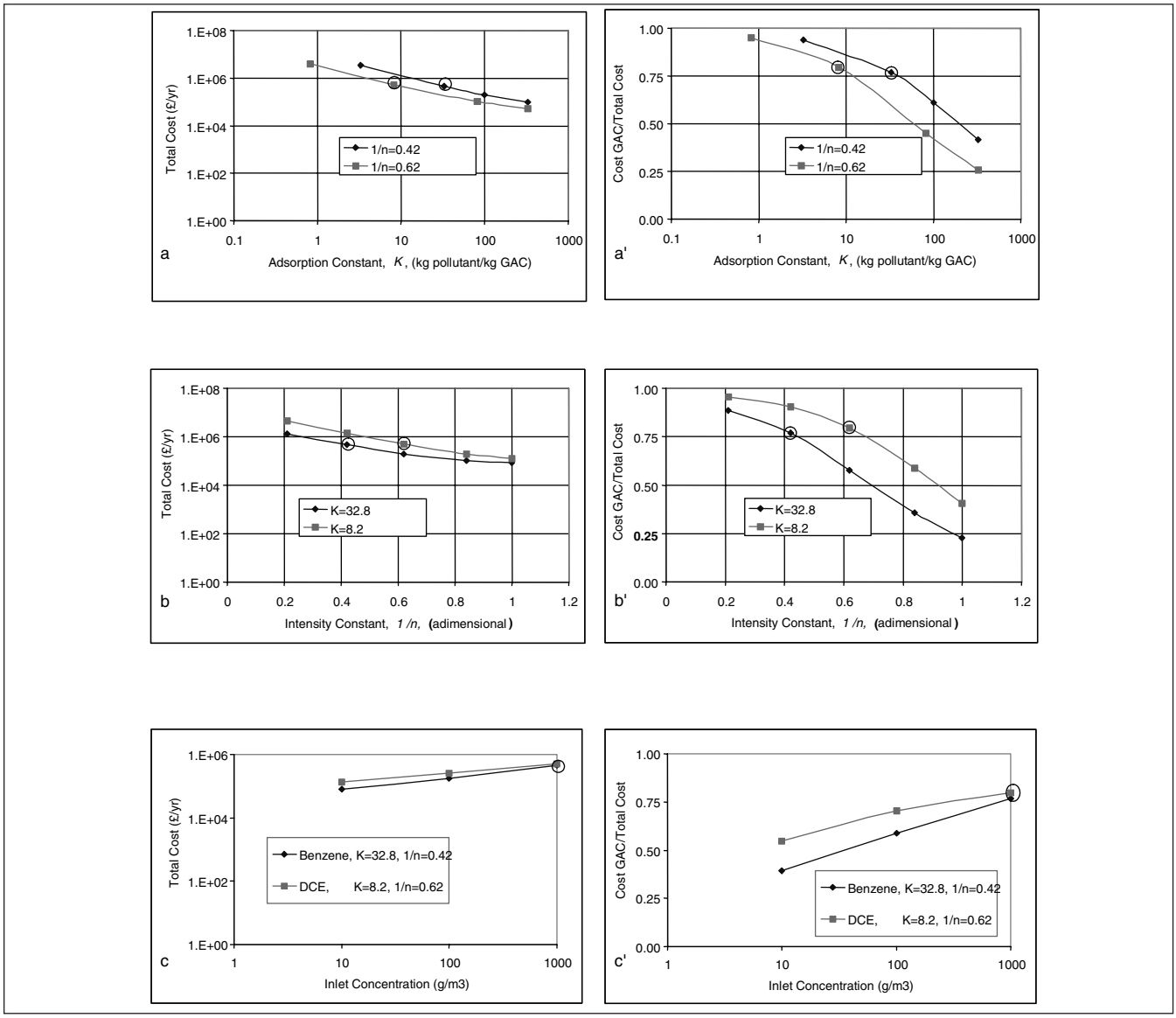

Fig. 4: Total treatment costs and the relative contribution of carbon requirements to total costs with respect to (a, a') the capacity constant, *K*; (b, b') the intensity constant, *1/n*, and; (c, c') the inlet concentration, C_{in}

1/*n* describes the sensitivity to concentration, which reflects the ease or difficulty of removing an organic compound from solution. These characteristics influence the amount of GAC required and hence, the column height, power requirements, and storage facilities.

In this model, varying the value of *K* between 3.28 and 328, (which comprises the *K* values for most VOC compounds), resulted in dramatic changes in the total costs of treatment, which varied between 3,400,000 and 99,000 £/yr, respectively. In addition, it was found that the cost of GAC may represent more than 94% of the total cost for organics with low capacity constants, while the treatment of organic with high capacity constants may incur in GAC cost, which are as low as 24% of total costs. The influence of *1/n* in treatment costs was studied for *1/n* values between zero and one, which is the valid range for the analytical solution presented in this model. However, it should be noted that there are organic compounds that present *1/n* values higher than unity. Higher values of *1/n* lead to (exponentially) lower GAC requirements. Accordingly, varying the intensity constant between 0.21 and 1.0 resulted in treatment cost of 1,360,000 and 86,000 £/yr, respectively. Therefore, vary small differences in the estimation of this parameter may change results dramatically. There is a direct relationship between the amount of GAC required and the inlet concentration, since the later represents – at a constant flowrate – the amount of pollutant fed into the process. As expected, varying C_{in} shows that low inlet concentrations – and low flowrates – can turn the GAC process into a very attractive wastewater treatment technology.

4 Inventory of Emissions

The emission of contaminants to the three environmental media was inventoried under an LCA approach, based on recommendations presented by Aelion, US Enviornmental Agency and SETAC [13,14,15]. Emissions produced through electricity generation, production-use-regeneration of granular activated carbon (GAC), and untreated pollutant, were all considered. Pollutant species involved within the system in this case example were: benzene or 1–2 dichloroethane which are removed from the wastewater stream (*Outputs*) and SO_2, Hydrocarbons (HC), NO_2, N_2O, CO, CO_2, associated with *Inputs* generation.

4.1 Emissions related to electricity generation

The amount of electricity consumed by the feed pump and two pump-eductor systems is correlated to emission factors, e.g., grams of pollutant per kWhr. This data is always calculated from the cost optimal process model previously described. Emission factors used for this work can be consulted in Sima Pro database [16].

4.2 Emissions related to GAC production, use and regeneration

Four stages have been identified in the life cycle assessment of GAC, as shown in **Fig. 5**. The first one describes those emissions associated with the production of raw materials. The second provides information of those pollutants discharged during transformation of raw materials into GAC. The third is related with the use of GAC for the wastewater treatment process and the fourth deals with the regeneration of the carbon.

4.2.1 Raw Materials

There are four basic raw materials considered for the production of GAC: water, coal, wood and coke. As an initial estimation, there are no emissions considered in this work for to the production of H_2O and wood, being that they are natural species in the environment. However, the reader should note that in a more detailed inventory of emissions, other activities such as pumping water and milling trees should be considered.

4.2.2 Production of GAC

A mixture of typical raw materials is assumed for the production of GAC [7]. It is comprised by 50% H_2O, 30% coal, 10% wood and 10% coke. **Fig. 6** describes the stages considered for the production of GAC from 1g of raw materials. The mixture is first burnt in order to evaporate the water, which inevitably burns off a portion of the organics, releasing CO_2 and H_2O. The use of external fuels for combustion is not considered since coal, wood and coke are combustible. The final product is 0.3g of GAC which is ready for use in the wastewater treatment process assumed [7].

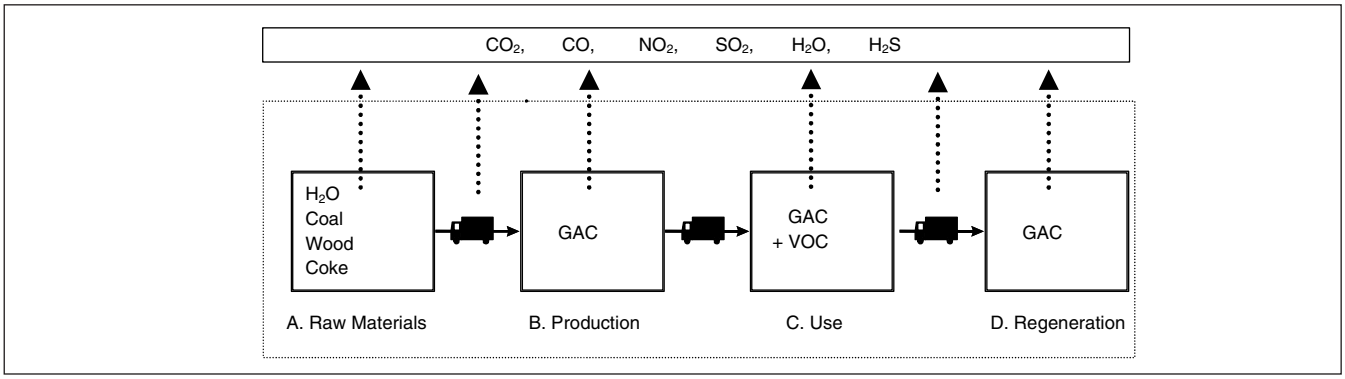

Fig. 5: Life cycle analysis of Granular Activated Carbon (GAC)

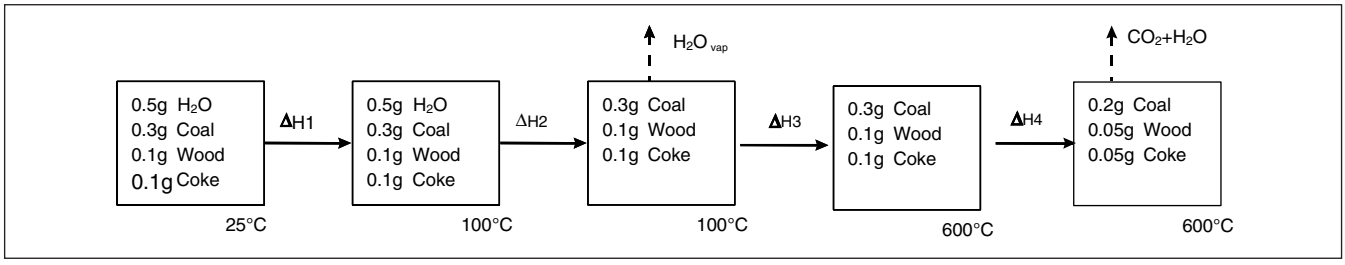

Fig. 6: Production of GAC at 30% conversion of raw materials

Mass Balances were performed in order to estimate emissions associated to the production of GAC. The chemical formulas of the three organics are used as a vehicle to calculate emissions related to combustion. It assumes: a basic model to describe the structure of coal; cellulose as the only structural component of trees and; *Continental No. 1* as the type of coke used for the process. Stoichiometric equations describing the combustion of coal, wood and coke were applied in order to perform mass and energy balances associated to the production of GAC as presented by Bailey J.E. et al and; the US National Research Council [17,18].

$$2\ C_{100}H_{70}O_{10}N_2 + 226\ O_2 \rightarrow 200\ CO_2 + 70\ H_2O + 2\ N_2O \quad (1)$$

Molecular weight of coal: 1458 g/mol. Therefore, combustion of 1g of coal leads to the following emissions: 2.744g CO_2, 0.432g H_20 and 0.0267g of NO_2.

$$2\ C_{18}H_{30}O_{16} + 35\ O_2 \rightarrow 36\ CO_2 + 30\ H_2O \quad (2)$$

Molecular weight of cellulose: 502 g/mol. Thus, combustion of 1g of wood leads to the following emissions: 3.168g CO_2 and 1.08g H_20.

$$C_{288}H_{28}N_8\ S_1 + 297\ O_2 \rightarrow 288\ CO_2 + 14\ H_2O + 8\ NO_2 + SO_2 \quad (3)$$

Molecular weight of coke: 3572 g/mol. Therefore, combustion of 1g of coke leads to the following emissions: 3.8g CO_2, 0.076g H20, 0.18g of NO_2 and 0.02g of SO_2.

4.2.3 Use of GAC

The use of GAC is described by the utilities required to run the GAC adsorption process. In this analysis, electricity highlights as the only source of emission. The inputs required for the process are calculated from the mathematical model of the process.

4.2.4 Regeneration of GAC

Information provided by Hutchins is used to calculate the amount of electricity and fuel consumed during the carbon regeneration process [19]. Correlations correspond to thermal reactivation, which is the most common technique used to regenerate GAC [20]. This work assumes a thermal regeneration plant with a typical capacity of 7,500 kg_{GAC} /day [19].

Mass and energy balances performed for the life cycle analysis of GAC are based on $1m^3$ of GAC, therefore, proper unit transformation and conversion factors have been applied for consistency. Emissions related to steel manufacture were found to be negligible since they are lower, by at least five orders of magnitude, than the rest.

Fig. 7 provides an indication of the type and amount of pollutants that may be discharged during the raw materials, production, use or regeneration stage in the GAC life cycle assessment. This figure suggests that carbon re-use may bring environmental benefits to the treatment process. The raw

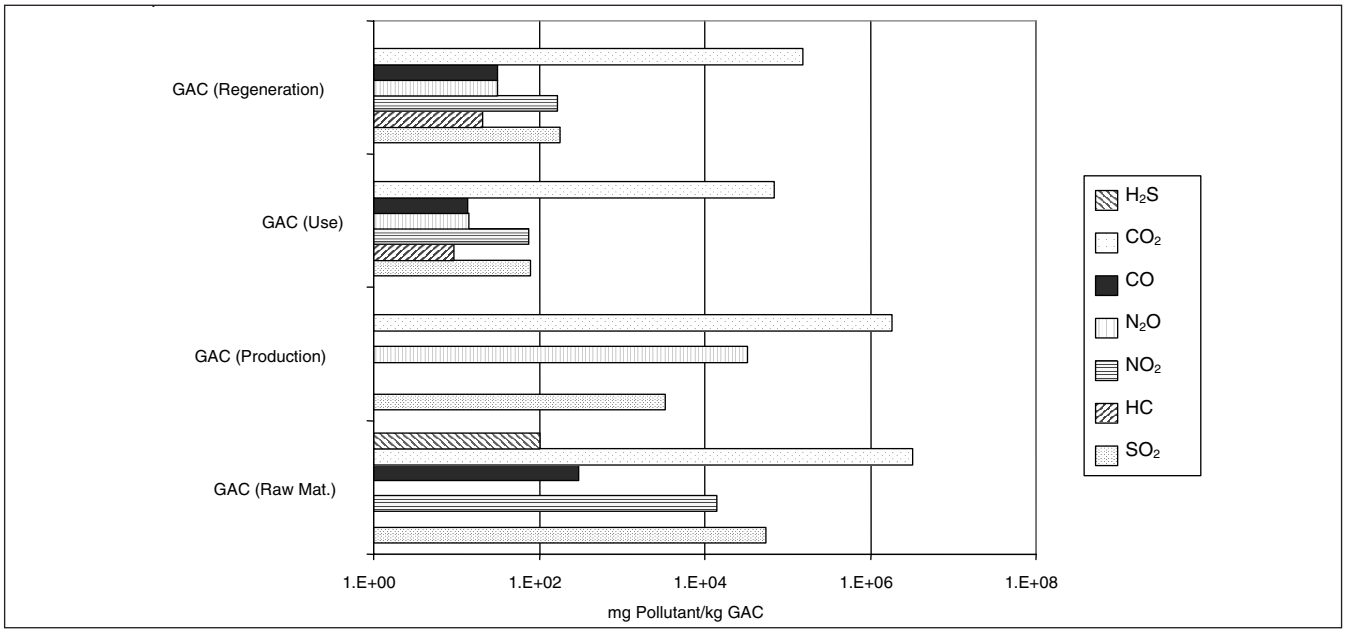

Fig. 7: Inventory of emissions derived from a life cycle assessment on the GAC

materials and the production stages create significantly more emissions of various pollutant species than those related to the use and regeneration of carbon. However, the inventory of emissions needs to be transformed into environmental impacts in order to gain insight into the environmental phenomena that may be caused by these emissions.

5 Environmental Impacts

Two environmental impacts, photochemical ozone creation (POC) and global warming potential (GWP), were incorporated into the process model in order to assess the environmental performance of the wastewater treatment processes, according to a standard methodology [21,22]. POC, also known as photochemical smog, reflects the ability of chemical compounds to react with NO and eventually form ozone, O_3. POC values are determined relative to emissions of the reference substance, ethylene [23]. GWP estimates the relative contribution of each pollutant, compared to carbon dioxide, to heat up the atmosphere (greenhouse effect) [24].

The possible benefits derived from the re-use of GAC are also explored in this section for three rates of re-use: 30, 60 and 90%. However, it is important to note that breakthrough curves developed for this process assuming that fresh carbon is used. This is due to the fact that breakthrough curves with regenerated carbon can only be reliably predicted by laboratory or pilot plant experiments. Thus, the adsorptive capacities of fresh and regenerated carbon are considered to be equal. The present model considers that in every regeneration, at least 10% of the GAC is lost due to attrition and that all the GAC (fresh and re-used) is exchanged for fresh carbon after one year. The price of new GAC is set at £1.42 per kg while the price for regenerated carbon is £1.12 per kg both of them being typical market values [7,8]. The environmental impacts of the system are described in the following sections.

POC impact evaluated for the GAC system is (slightly) lower for benzene than for DCE, as shown in **Fig. 8**. However, the POC impact of the untreated benzene and DCE discharges, presented on the ordinate axes, shows that benzene causes a higher POC impact. Treatment of benzene requires lower electricity and activated carbon, and thus generates lower POC impact than the treatment of DCE. Since the carbon adsorption process removes 100% of the benzene and DCE, the POC impact presented in Fig. 8 is due only to Inputs. It should be noted that the POC impact associated with process

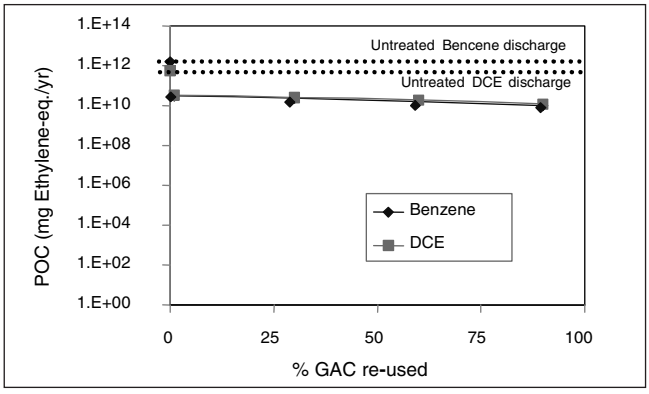

Fig. 8: POC impact of the carbon adsorption process, operating at various degrees of carbon re-used

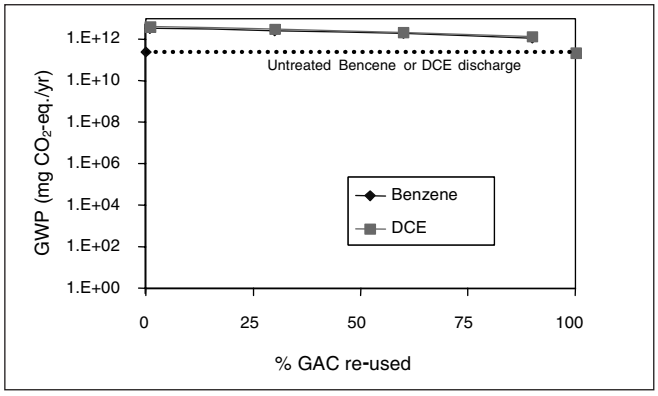

Fig. 9: GWP impact of the carbon adsorption process, operating at various degrees of carbon re-used

Inputs is significantly lower than the POC impact caused by an untreated wastewater discharge, even if more than 250 tonnes of carbon are consumed per year of operation. Viewed another way, setting up a carbon adsorption process to remove benzene provides considerable environmental benefits as shown in Fig. 8, where the environmental impact of the untreated benzene discharge, plotted on the ordinate axes, is significantly higher than the corresponding environmental impact, when the treatment technology is used. This figure also shows that higher rates of GAC re-use lead to lower POC impacts. As such, avoiding the acquisition of raw materials and the production of new GAC via carbon regeneration and re-use is found to be more environmentally friendly.

Fig. 9 shows the GWP impact with respect to both organics. Note that the environmental impact of the benzene and DCE untreated discharges is shown on the ordinate axes. Values are equivalent for both organics since the global warming index is the same for benzene and DCE. The environmental analysis, based on global warming impact, shows that the GAC process is not an effective option for the removal of benzene or DCE, if reduction of global warming is the goal. Setting up and operating a GAC treatment plant causes higher environmental impact than an untreated wastewater discharge! This is consistent for both the benzene and the DCE wastewater streams. Hence, treatment of benzene or DCE results in both higher environmental impact and unnecessary treatment costs.

6 Discussion

Technology assessment is a every day issue that involves not only industries but also policy makers. This paper has illustrated the use of life cycle and process engineering tools to assess the sustainability of a clean-up technology. The general framework presented in this work is mathematically robust so that it can easily be adapted into almost any other kind of technology. One of the main advantages of this framework is that it is focused on optimising the design and operation of a process as opposed to only evaluating some design scenarios. Furthermore, it highlights the importance of understanding the physical and chemical phenomena associated to a process so that it can be properly described and related to other cost factors. This assessment included a mathematical model for process design, and considerations towards economic, and environmental impacts.

Specifically, a typical wastewater treatment technology, carbon adsorption (GAC), and two different chemical waste streams have been used as a motivating example. The mathematical model of the process and its consequent optimal design provided an understanding of the process operation and performance. These findings can be used to compare other technology alternatives or process designs on a cost optimised basis. Benzene and DCE compounds cause different effects on the carbon adsorption treatment process. Treatment costs are lower for the former while total POC and GWP environmental impact is slightly higher for the latter. These results were consistent even under the assumption of an ideal adsorption isotherm.

The mathematical cost optimised model provided economic and environmental information of one of the most common adsorption configurations for industrial wastewater treatment. However, there are several possible configurations that can be applied to the carbon adsorption process ranging from the type of operation (batch or continuous), the type of carbon (powered or granular), and the type and location of carbon regeneration (steam or thermal reactivation; in- or off-site). The optimal process configuration is case specific and depends of factors such as flowrate, type and concentration of pollutants, carbon re-use rate, and degrees of removal. Hence, the best design option in terms of economics and environmental impact can only be identified by applying a life cycle analysis approach for each process alternative.

The findings presented in this work have serious implications for environmental policy makers on the use of LCA as opposed to traditional feasibility studies. A traditional approach, applied to treatment technologies, would tell that higher degrees of wastewater pollution abatement always lead to lower environmental impacts. Therefore, the degree of abatement should be as high as possible, while costs should not be excessive. This approach only guarantees a reduction of emissions *within* the process. In contrast, a LCA approach demonstrates that under certain conditions, higher degrees of wastewater pollution abatement worsen the environment, and probably worst, unnecessary demand the implementation of treatment technologies. Moreover, this work shows that environmental solutions, such as treatment technologies, may produce a higher environmental impact than the one that can be caused by untreated discharges, as shown in the GWP assessment.

The economic and the environmental implications (measured in terms of GWP) of the GAC treatment plant discourage the acquisition of this technology. However, policy makers should also be aware of the social implications, which in this case study would change the picture. A social evaluation, measured in terms of hazard, would demonstrate that adverse effects occur and therefore, the implementation of the designed technology was morally and legally mandatory.

There is still significant work to be done in order to combine process engineering and LCA tools. However, this paper suggests that environmental policy makers and industries can use a similar approach for evaluating various technologies. Most processes and technologies include information regarding physical and chemical phenomena so developing a mathematical model to describe economic and environmental performance is relatively straight. The advantages of mathematical modelling allow it to be applied into other areas such as process design and development, green chemistry and technology management.

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Appendix A (Online only: http://dx.doi.org/10.1065/lca2004.09.180.11)

Granular Activated Carbon Adsorption. Process Design and Modelling:

Determination of the main equipment size

Adsorber Column. The volume of the adsorber column can be estimated through the following expression:

$$V_{ads} = A_t . H \tag{A.1}$$

According to Faust and Aly, (1987), the height of the adsorber column, H, should be higher than 1.35 m in order to accommodate a packed bed long enough to ensure formation of a constant pattern. In addition, a maximum height of 18.5 m should be attained to ensure shipment safety limitations.

The volume of the adsorber, should account for bed expansion and maintenance, thus, the activated carbon occupies 66% of the total adsorber column, giving rise to the following expression:

$$V_{ads} = 1.5.V_{bed} \tag{A.2}$$

Hand et al. (1984) developed an expression that is able to calculate the capacity of the bed, before breakthrough or saturation occurs. This accounts for the unsteady state nature of the adsorber column, pollutant characteristics, flow, solid-liquid equilibrium relationships and the type of GAC selected for the process. The homogeneous surface diffusion model (HSDM) presented by Hand et al.(1984), has successfully predicted fixed-bed adsorber dynamics for over 100 adsorbate-adsorbent systems, including potentially harmful organics such as benzene and toluene.

The model relies on a set of dynamic equations that model an adsorption system and have been solved analytically to generate algebraic equations. In order to achieve an exact solution of the equations, the following assumptions must be incorporated into the model: (1) plug flow exists in the bed, which was confirmed to be valid as long as the mass transfer zone is longer than 30 adsorbent particle diameters, and is supported by Miyachi and Kikuchi (1975) and Stenzel (1993); (2) the hydraulic loading (inlet flowrate) is constant; (3) surface diffusion is the predominant intraparticle mass transfer mechanism and is not a function of concentration; (4) the local liquid-phase mass transfer rate can be described by the linear driving force approximation; (5) the adsorbent is in a fixed position in the adsorber and is considered to be spherical; and (6) the adsorption equilibrium can be described by the Freundlich isotherm. The analytical solution to the HSDM for the case in which liquid-phase mass transfer controls the adsorption rate and $1/n$ is less than 1.0 has been developed by Fleck (1973) and presented by Hand et al. (1984).

$$T = \frac{D_g}{3.St.\left(D_g + 1\right)}\left[1 + \ln\left(\frac{C_{out}}{C_{in}}\right) - \left(n-1\right).\ln\left(1 - \frac{C_{out}}{C_{in}}\right)^{\frac{1}{n-1}} + \gamma\right] + 1 \tag{A.3}$$

in which, n is the Freundlich isotherm intensity constant, and

$$\gamma = \frac{\frac{1}{n}}{\left(\frac{1}{n} - 1\right)} \sum_{k=1}^{\infty} \frac{\frac{1}{n}}{k\left(k1 - \frac{1}{n} + \frac{1}{n}\right)} \tag{A.4}$$

Mass throughput, T, is defined as the ratio of mass fed compared to the mass required to saturate the adsorber. The dimensionless time scale, mass throughput, is defined (Hand et al. 1984) as:

$$T = \frac{Time}{\tau.\left(D_g + 1\right)} \tag{A.5}$$

The solute distribution parameter, D_g, is defined as the ratio of the mass of adsorbate in the solid-phase to the mass of adsorbate in the liquid-phase under equilibrium conditions. This parameter is calculated from the following expression:

$$D_g = \frac{\rho_p . q^* \left(1 - \varepsilon\right)}{\varepsilon . C_{in}} \tag{A.6}$$

The particle density, ρ_p, and the void fraction, ε are parameters that depend on the type of GAC employed. These calculations assume the use of Calgon Filtrasorb 300 as carbon adsorbent.

Liquid-solid equilibrium between the concentration of pollutant adsorbed on the carbon surface and the concentration of pollutant in the untreated wastewater, q^*, is described by the Freundlich isotherm.

$$q^* = K.C_{in}^{\,1/n} \tag{A.7}$$

Both the capacity constant, K, and the intensity constant, $1/n$, are solute specific and are available in several publications. The values used for this model are those presented by Faust and Aly (1987).

The void fraction of the packed bed, ε, depends on both the apparent density, ρ_a, and the particle density, ρ_p, of the activated carbon. Thus, it can be described by the following expression:

$$\varepsilon = 1 - \frac{\rho_a}{\rho_p} \tag{A.8}$$

The Stanton number, S_t, is a measure of the bed length as compared to the length of the mass transfer zone for the case in which the liquid-phase mass transfer resistance controls the adsorption rate.

$$S_t = \frac{k_f . \tau . \left(1 - \varepsilon\right)}{R.\varepsilon.\phi} \tag{A.9}$$

This expression depends on the characteristics of the GAC employed. Two new parameters are introduced, the mean particle ratio, R, and the sphericity, ϕ, that accounts for the ratio of surface area of equivalent-volume sphere to actual surface area of adsorbent particle (dimensionless). The later value can be taken from Perry (1984), whereas the particle ratio can be read from Faust and Aly (1987).

The packed bed contact time, τ, also known as fluid residence time in the packed bed, is defined as the quotient of the free bed volume available for liquid flow divided by the wastewater flowrate through the bed.

$$\tau = \frac{\varepsilon . V_{bed}}{Q} \tag{A.10}$$

The mass transfer coefficient for the liquid film, k_f, is based on a correlation presented by Crittenden et al. (1978).

$$k_f = \frac{2.40.v_s}{Re^{0.66}.Sc^{0.58}} \tag{A.11}$$

This correlation is valid for Reynolds numbers, *Re*, ranging between 0.08 and 150, and Schmidt numbers, *Sc*, between 150 and 1300, which are broad enough to cover the liquid loading applied for this model.

The Reynolds number is calculated from information related to the density and viscosity of the wastewater stream, which is assumed to be equal to those of pure water due to the low concentration of organics present.

$$Re = \frac{R.v_s.\rho}{\varepsilon.\mu} \tag{A.12}$$

The Schmidt number is also related to the fluid viscosity, density and diffusivity of pollutants in water, as expressed below.

$$Sc = \frac{\mu}{\rho.D_{wat}} \tag{A.13}$$

The superficial liquid velocity, v_s, is calculated based on the cross sectional area of the adsorption column.

$$v_s = \frac{Q}{A_t} \tag{A.14}$$

The adsorption column is subject to a pressure drop, which depends on the superficial liquid velocity, the height of the column and some properties of the GAC. A empirical correlation developed by Leva (1949) is used for its estimation. It applies for laminar flow, with Reynolds numbers below 20 and has been supported by extensive data ranging from runs performed with GAC, sands and particles, including Berl saddles and complex ring packing.

$$\Delta P_{ads} = \frac{2.5706.10^{-11}.v_s.H.\mu.(1-\varepsilon)^2}{\phi^2.R^2.\varepsilon^3} \tag{A.15}$$

Eductor and Pumps. As previously mentioned, this process uses eductors to transport GAC. The system employs water as motive pumping fluid in order to create a slurry which can be easily transport. Therefore, this model considers the use of one pump for the inlet flow, that provides liquid to the eductors, and a hopper, which feeds the new, and the exhausted GAC. The empirical correlation presented by Perry (1984) is used to calculate power requirements for the pumps. Equations for the wastewater inlet flow and the two pump-eductor systems are presented below.

$$W_{Pu-WW} = \frac{3.Q.(\Delta P_{ads} + 0.0097.H)}{36.\eta} \tag{A.16}$$

$$W_{Pu-F-Ed} = \frac{FW_{Pu-F-Ed}.P_{D-F-Ed}}{36000.\eta} \tag{A.17}$$

$$W_{Pu-S-Ed} = \frac{FW_{Pu-S-Ed}.P_{D-S-Ed}}{36000.\eta} \tag{A.18}$$

The discharge pressure, process water requirements and suction capacity of GAC for the feed carbon pump-eductor system were obtained from regressions of operating data presented by Karassik (1976), where these quantities are related to the discharge pressure of the eductor.

The discharge pressure for the spent eductor pump, process water requirements and suction capacity for the spent carbon eductor are read from tables provided by Karassik (1976), which in turn, follow recommendations given by Culp and Clark (1983) for carbon handling.

The number of carbon changes required per year determines the operating times of the individual eductors. This time is defined by the yearly operational time, the time for pollutant breakthrough, and the time required to exchange exhausted for fresh GAC, which is defined as the quotient between the packed bed volume and the suction capacity of the eductor.

$$OpTime_{Pu-F-Ed} = \frac{OpTime.V_{bed}}{Time.SC_{F-Ed}} \tag{A.19}$$

$$OpTime_{Pu-S-Ed} = \frac{OpTime.V_{bed}}{Time.SC_{S-Ed}} \tag{A.20}$$

Carbon Regeneration/Exchange. Carbon Exchange is often the most critical parameter of the adsorption system operation and may be the predominant component of the operating costs, as well as the key to safe disposal of the organic contaminants removed from the process. This model assumes that carbon exchange takes place once breakthrough occurs. This assumption is necessary in order to estimate the carbon requirements and to avoid exchange zone amplifications between both adsorbers which would require experimental data and therefore limit the flexibility of the model. This assumption is supported by the type or organic compounds to be removed, which produce sharp breakthrough curves, implying almost complete exhaustion of the bed when breakthrough occurs. Spent carbon can be landfilled or incinerated as a solid waste. Coal-based granular activated carbon, however, is usually reactivated. The reactivation process drives off the more volatile organic compounds from the carbon surface and pyrolyses and decomposes less volatile compounds held within the pores (Cheremisinoff and Ellerbush 1978). Reactivation has proven to be a safe and cost-effective means to destroy adsorbed organic compounds and allow reuse of the carbon.

Cost equations The total treatment cost is a function of the capital and operating cost.

$$C_t = C_o + C_c \tag{A.21}$$

The equipment contributing to the capital cost is seen on the flowsheet; i. e., 2 adsorber columns, the wastewater pump, two pump-eductor systems for carbon transportation, and two storage tanks for fresh and exhausted GAC.

$$C_c = bm \cdot dep \cdot (2.C_{Ads} + C_{Pu-WW} + C_{Pu-F-Ed} + C_{Pu-S-Ed} + 2.C_{Tank}) \tag{A.22}$$

The operating costs are a function of the electricity consumed to run the process pumps, water required to transport the GAC and replacement of GAC employed for the process. **Note:** The regeneration costs are not considered in the economic model since it is performed off-site.

$$C_o = C_{el} + C_w + C_{GAC} \tag{A.23}$$

The cost of the adsorber column is calculated from recommendations given by Guthrie (1969) and Douglas (1988). Stainless steel is considered as the material for construction in order to resist the reaction that may be caused by the presence of GAC, organics and water (Stenzel 1993).

$$C_{Ads} = 101.9\left(\frac{MS_{95}}{MS_{68}}\right).(6.5616.R_{Ads})^{1.066}(3.2808.H)^{0.82}.(3.67) \quad (A.24)$$

Similar equations, based on recommendations given by Walas and Spangler (1960), are used to estimate the cost of the pumps in the system.

$$C_{Pu} = 655.82\left(\frac{MS_{95}}{MS_{59}}\right)(1.341.W_{Pu})^{0.4918} \quad (A.25)$$

The cost of the storage tanks for fresh and exhausted GAC is calculated, from recommendations given by Stenzel (1993). GAC supply is carried out four times a year. Therefore, it is assumed that the volume of each storage tank is 25% of the total GAC required per year. The following equation results from a linear regression of the plot presented in Institute Francais du Petrole (1976), for storage tanks at atmospheric pressure with stainless steel as construction material.

$$C_{Tank} = 2\left(\frac{MS_{95}}{MS_{68}}\right)\left[2570.LN(0.25.V_{Bed}.OpTime/Time)+3100\right] \quad (A.26)$$

Process pumps are the primary power consumers. In this process, only the wastewater feed pump operates continuously, while the eductor pumps operate intermittently for charging and discharging GAC in the adsorber columns. The specific costs for electricity, water and GAC were obtained from Peters and Timmerhaus (1980) and updated according to the Marshall and Swift Index.

$$Cel = SC_{el}\left(W_{Pu-WW}.OpTime + W_{Pu-F-Ed}.Op - Time_{Pu-F-Ed} + W_{Pu-S-Ed}.Op - Time_{Pu-S-Ed}\right) \quad (A.27)$$

The cost of water used for the eductors is calculated as follows:

$$C_w = SC_w\left(FW_{Pu-F-Ed}.OpTime_{Pu-F-Ed} + FW_{Pu-S-Ed}.OpTime_{Pu-S-Ed}\right) \quad (A.28)$$

The cost of the GAC is calculated as a function of the packed bed volume and the number of loads required per year of operation.

$$C_{GAC} = SC_{GAC}\left(\frac{OpTime}{Time}\right).V_{Bed} \quad (A.29)$$

List of Symbols: Carbon Adsorption

A_t	Sectional Area of Adsorber Column	m^2
C_{Ads}	Cost of Adsorber Column	£/yr
Cc	Capital Cost of the Process	£/yr
C_{el}	Cost of electricity	£/yr
C_{GAC}	Cost of Granular Activated Carbon	£/yr
C_{in}	Inlet Pollutant Concentration	kg/m^3
Co	Operating Cost of the Process	£/yr
C_{out}	Outlet Pollutant Concentration	kg/m^3
$C_{Pu\text{-}F\text{-}Ed}$	Cost of Pump-Eductor Feed GAC System	£/yr
$C_{Pu\text{-}S\text{-}Ed}$	Cost of Pump-Eductor Spent GAC System	£/yr
$C_{Pu\text{-}WW}$	Cost of Wastewater Inlet Pump	£/yr
Ct	Total Cost of the Process	£/yr
C_w	Cost of water for the GAC pump-eductor systems	£/yr
dep	Capital charge factor	yr^{-1}
D_g	Solute Distribution Parameter	–
D_{wat}	Diffusivity of Organic in Water	m^2/hr
$FW_{Pu\text{-}F\text{-}Ed}$	Flow of water for the Pump-Eductor Feed GAC System	kg/hr
$FW_{Pu\text{-}S\text{-}Ed}$	Flow of water for the Pump-Eductor Spent GAC System	kg/hr
H	Height of the Adsorber Column	m
K	Freundlich Isotherm Capacity Constant	mg/g
k_f	Liquid Film Mass Transfer Coefficient	m/hr
MS_{59}	Marshall and Swift Index 1959	–
MS_{68}	Marshall and Swift Index 1968	–
MS_{95}	Marshall and Swift Index 1995	–
N	Freundlich Isotherm Intensity Constant	–
$OpTime$	Operating Time for the Process	hr
$Op\text{-}Time_{Pu\text{-}F\text{-}Ed}$	Operating Time for the Pump-Eductor Feed GAC System	hr
$Op\text{-}Time_{Pu\text{-}S\text{-}Ed}$	Operating Time for the Pump-Eductor Spent GAC System	hr
$P_{D\text{-}F\text{-}Ed}$	Discharge Pressure for the Feed GAC Eductor	bar
$P_{Pu\text{-}S\text{-}Ed}$	Discharge Pressure for the Spent GAC Eductor	bar
Q	Wastewater Flowrate	m^3/hr
q^*	Equilibrium concentration between solid phase and inlet liquid	kg/kg
R	GAC Mean Particle Ratio	m
R_{ads}	Ratio of the Adsorber Column	m^2
Re	Reynolds Number	–
Sc	Schmidt Number	–
SC	Suction Capacity	m^3/hr
SC_{el}	Specific Cost of Electricity	£/KW.hr
SC_{GAC}	Specific Cost of GAC	$£/m^3$
SC_w	Specific Cost of Water	$£/m^3$
St	Stanton Number	
T	Mass Throughput	–
$Time_{GAC}$	Elapsed time for the GAC	hr
V_{Ads}	Volume of the Adsorber Column	m^3
V_{Bed}	Volume of the Bed	m^3
v_s	Superficial Liquid Velocity	m/hr
$W_{Pu\text{-}F\text{-}Ed}$	Power of the Pump-Eductor Feed GAC System	kW
$W_{Pu\text{-}S\text{-}Ed}$	Power of the Pump-Eductor Spent GAC System	kW
$W_{Pu\text{-}WW}$	Power of the Wastewater Inlet Pump	kW
ΔP_{Ads}	Pressure Drop Through Adsorber Column	bar
ε	Void Fraction of Packed Bed	–
ϕ	Sphericity of the GAC particle	–
γ	Series factor for the Throughput Equation	–
η	Pump Efficiency	–
μ	Viscosity of Water	kg/m.hr
ρ	Density of Water	kg/m^3
ρ_a	Apparent Density of the GAC Particle	kg/m^3
ρ_{pa}	Density of the GAC particle	kg/m^3
τ	Residence Time for the Fluid in Packed Bed	hr